UCRL- 85483
PREPRINT

PHASE EQUILIBRIA, LEACHING CHARACTERISTICS AND CERAMIC PROCESSING OF SYNROC D FORMULATIONS FOR U.S. DEFENSE WASTES

H. Newkirk
F. Ryerson
D. Coles
C. Hoenig
R. Rozsa
C. Rossington
F. Bazan
J. Tewhey

This paper was prepared for submittal to
Materials Research Society Annual Meeting
Boston, Massachusetts, November 16-20, 1980

Lawrence Livermore Laboratory

DISCLAIMER

PHASE EQUILIBRIA, LEACHING CHARACTERISTICS AND CERAMIC PROCESSING OF SYNROC D FORMULATIONS FOR U.S. DEFENSE WASTES*

H. Newkirk, F. Ryerson, D. Coles, C. Hoenig,
R. Rozsa, C. Rossington, F. Bazan, and J. Tewhey

Lawrence Livermore National Laboratory
Livermore, California 94550

INTRODUCTION

High-level U.S. defense wastes consist of reprocessed wastes which have been neutralized with excess NaOH. The neutralization process has resulted in the precipitation of an insoluble sludge containing most of the radionuclides except cesium, which is present in a supernatant salt solution. Defense wastes have been generated by a variety of reactor and separations processes, therefore, they tend to be compositionally heterogeneous.

The SYNROC concept, as applied to commercial high-level nuclear waste, was introduced by Ringwood in 1978[1]. The SYNROC formulation for immobilization of commercial wastes, designated SYNROC C, consists of the three-phase assemblage, hollandite ($BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$), and zirconolite ($CaZrTi_2O_7$). An alternative SYNROC formulation for the immobilization of high-level defense wastes, designated SYNROC D, was proposed by Ringwood in 1979[2,3]. The assemblage of coexisting phases in SYNROC D are perovskite, zirconolite, nepheline ($NaAlSiO_4$) and spinel ($R^{2+}O \cdot R_2^{3+}O_3$). Cesium from the supernate is to be immobilized in hollandite. In the current processing scheme, presynthesized granules of hollandite will be added to calcined SYNROC D powders prior to hot processing or sintering.

DISPOSITION OF DEFENSE WASTES COMPONENTS IN SYNROC D

The major components of Savannah River Plant (SRP) sludge calcines and their tank-to-tank limits of variation are given below[4]. The principal radwaste components in the sludge are fission products; ^{90}Sr,

* Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-eng-48.

^{147}Pm, ^{137}Cs, ^{151}Sm, ^{134}Ce, and ^{144}Ce. The principal alpha emitters are ^{238}Pu, ^{241}Pu, ^{239}Pu, ^{240}Pu, and ^{244}Cm although the gross alpha level is low, 0.5 mCi/gallon of sludge[5]. ^{137}Cs is the major radwaste component in the supernate.

Component Average Composition		Limits of Variation (wt%)
Fe_2O_3	5.8 - 57.7	39.4
Al_2O_3	5.3 - 83.4	30.9
MnO_2	3.9 - 10.9+	10.9
U_3O_8	1.4 - 13.4	3.6
CaO	0.4 - 3.9	2.9
NiO	0.9 - 9.9	4.9
SiO_2	0.4 - 0.9+	0.9
Na_2O	2.2 - 5.6+	5.6
Na_2SO_4	0.5 - 1.0+	1.0
		100.1

The disposition of inert and radwaste components of SRP wastes in SYNROC D formulations has been determined by means of optical microscopy, XRD, XRF, SEM, STEM, electron microprobe analysis and autoradiography. A summary of results are presented herein.

Sodium

Although sodium is present in SRP sludges in relatively small amounts, it is of some concern to SYNROC developers because it does not exhibit extensive solid solution in the titanate or spinel phases of SYNROC D. The important criteria for a suitable sodium host are that it be (1) thermodynamically compatible with the SYNROC D phase assemblage, (2) exhibit a resistance to leaching, and (3) require a minimum of additive components for its formation. Nepheline appears to fulfill these criteria. Nepheline contains $\approx$22 wt% sodium, therefore, a SYNROC D formulation consisting of 25% nepheline will immobilize the 5.6% sodium present in an average sludge. Nepheline stoichiometry requires the addition of silica at a 2:1 wt ratio to sodium and, in the case of alumina-deficient sludges, small additions of Al_2O_3. Experimental work at Australian National University (ANU) has shown that sodium can be effectively immobilized in rare earth or niobium perovskites ($Na_{.5}REE_{.5}TiO_3$ or $NaNbO_3$) if the sodium content of the sludge is <2 wt%[6].

Uranium and Other Actinides

Uranium replaces Zr in zirconolite, forming a $CaUTi_2O_7$ component. Uranium can also replace Ca in zirconolite or perovskite with charge balance achieved by substitution of Al^{3+} and/ or Fe^{2+} for Ti^{4+}. Actinide-doping experiments on SYNROC C formulations with ^{239}Pu, ^{241}Am, and ^{244}Cm have been done at Oak Ridge National Laboratory. Alpha autoradiography analysis has shown the actinides to be equally partitioned in zirconolite and perovskite. The other coexisting SYNROC phases were found to be actinide-free[7]. Rare earth elements are also partitioned equally between zirconolite and perovskite.

Strontium

In SYNROC C and SYNROC D formulations, Sr is strongly partitioned into perovskite with lesser amounts going into zirconolite. Experiments at ANU with a two-phase SYNROC formulation (perovskite absent) have shown that zirconolite can accept up to 1.4 wt% Sr into solid solution. SYNROC D formulations made from SRP sludges containing >10 wt% U_3O_8 will have high percentages of zirconolite and minor perovskite. Zirconolite will be the principal host for Sr in waste forms with high U content.

Cesium

The small amount of Cs that is present in SRP sludge is partitioned into a silicate phase. Cs has been observed in dilute solid solution in nepheline and as tiny, discrete blebs of pollucite ($CsAlSiO_6$) coexisting with nepheline. In the processing scheme currently being developed for SYNROC D, the Cs from the supernatant solution will be incorporated into hollandite. In current experiments, 15 wt% of presynthesized hollandite containing 3.4 wt% Cs is added in millimeter sized "chunks" to SYNROC D (Fig. 1a, b). The Cs concentration in the final waste form is 0.5 wt%. These Cs concentrations have not been "optimized" and are subject to change based on phase equilibria and production technology criteria.

Iron, Aluminum, Manganese, and Nickel

Fe, Al, Mn, and Ni are the principal inert components in SRP sludge, collectively comprising from 75 to 95 wt% of the sludge. Each of these components can exhibit order-of-magnitude variation from tank to tank. The inert components form spinel solid solutions which can comprise as much as 60% of the final waste form. Titanium is also present as an ulvospinel component ($2R^{2+}O \cdot TiO_2$) in solid solution. Heat treatment and processing of SYNROC D near the Ni-NiO buffer ($f_{O_2} = 10^{-9.5}$ at 1050°C) is within the magnetite ($FeO \cdot Fe_2O_3$) field, thereby facilitating the synthesis of spinels. As a consequence of extensive solid solution between end-members, spinel is a "forgiving" phase in SYNROC D. The principal role of the SYNROC additives in SYNROC D formulations is to synthesize the radwaste-containing phases. That being the case, the amounts and proportions of additives are similar for the wide variety of SRP sludge compositions. The major inert components in the sludge are relatively insensitive to the additive components (except TiO_2) and end up as a complex spinel solid solution that is compatible with the bulk chemistry of the sludge (Fig. 2).

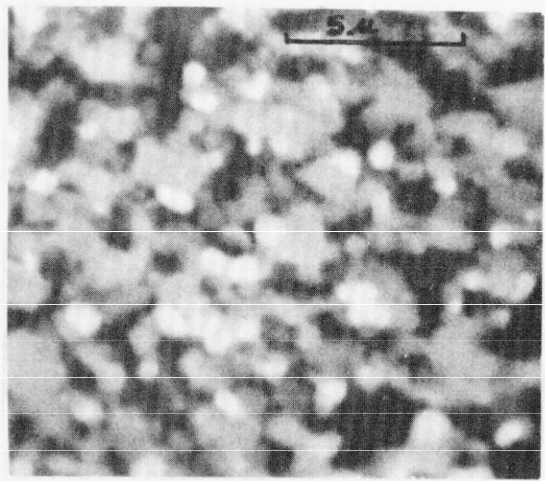

Fig. 1a. SEM photomicrograph of SYNROC D microstructure. Phases present are zirconolite (white), perovskite (medium gray euhedral crystals), spinel (medium gray irregular crystals) and nepheline (black). Scale bar at upper right is 5 microns.

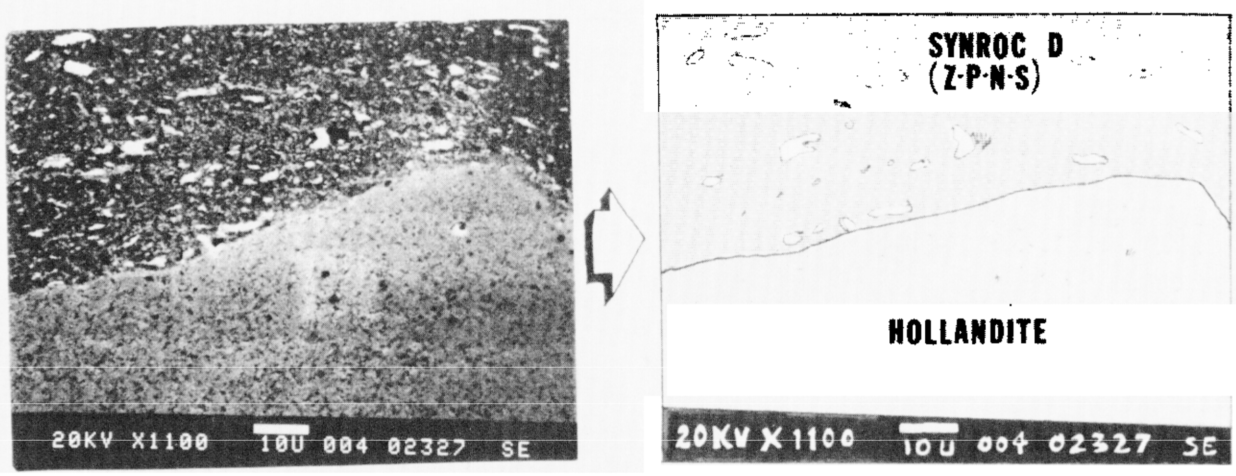

Fig. 1b. SEM photomicrograph of SYNROC D with granule of presynthesized hollandite. Matrix of SYNROC D consists of zirconolite, perovskite, spinel, nepheline and nickel metal. Scale bar is 10 microns.

SPINEL COMPOSITIONS IN SYNROC D

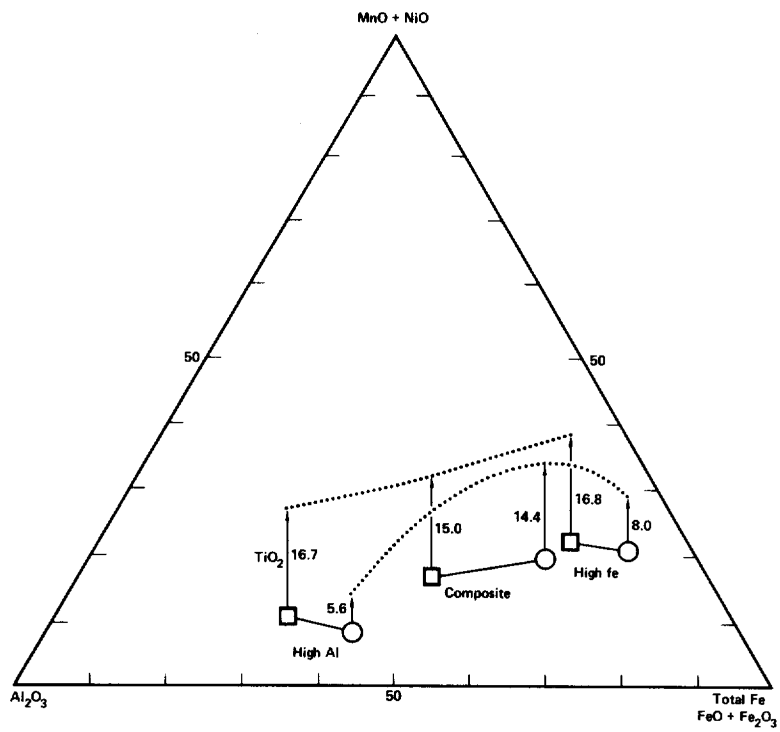

Fig. 2. Bulk chemistry of three SRP sludges plus SYNROC additives (squares) and the corresponding spinel compositions (circles) are plotted with respect to Al_2O_3 - (FeO + Fe_2O_3) - (MnO + NiO). Spinel compositions are iron-rich with respect to bulk compositions because aluminum goes into nepheline and zirconolite. TiO_2 content of spinels and sludge/ SYNROC D calcine are indicated graphically (arrows) and numerically. Spinels have a wide compositional range and are considered to be a "forgiving" phase.

SYNROC Additives

The principal SYNROC additives in SYNROC D formulations are TiO_2, ZrO_2, SiO_2, CaO, and in the case of the extreme compositions, Fe_2O or Al_2O_3. The latter are added to assure the synthesis of spinel. A small amount of Ni powder is added as a "getter" for excess oxygen. The amount of additives is dependent on (1) sodium content of the sludge, (2) uranium content and the level of uranium loading in zirconolite, and (3) an arbitrary zirconolite/perovskite ratio. A fixed amount of TiO_2 is added for incorporation into the spinel-ulvospinel$_{ss}$ (Fig. 3).

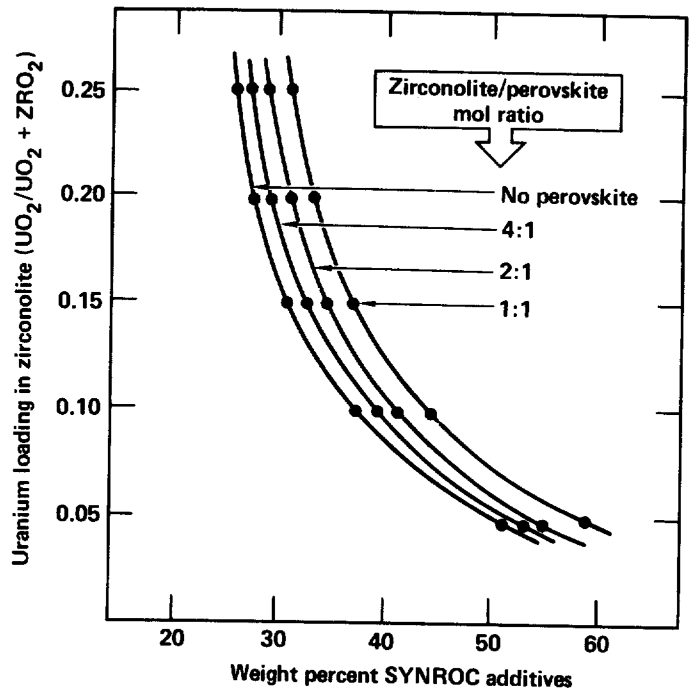

Fig. 3. Weight percent SYNROC D additives for SRP composite sludge plotted as a function of uranium loading in zirconolite and the desired zirconolite/perovskite ratio. Additives are TiO_2 (Z,P, spinel), CaO (Z,P), ZrO_2 (Z), and SiO_2 (nepheline).

LEACHING OF SYNROC D

Leaching studies of SYNROC D have been done by means of static, high temperature experiments and continuous-flow experiments (MCC-4)[8]. The data reported in Table 1 are from high-temperature experiments (distilled water, powdered sample, 150°C, one day). The elements reported are the only ones observed in the leachate. Analysis was done by means of XRF.

Table 1. Leaching Results of SYNROC D and Cs-Bearing Hollandite

Leach rate = g SYNROC or hollandite/m^2 · day

	Ca	Sr	U	Cs
SYNROC D (Z,P,N,S)	$<8 \times 10^{-3}$	7×10^{-4}	$< 1 \times 10^{-4}$	
Cs-Bearing Hollandite				7.8×10^{-3}

CERAMIC PROCESSING OF SYNROC D

The flow sheet in Figure 4 depicts the current experimental methods that are being employed at LLNL to produce SYNROC D samples containing presynthesized Cs-bearing hollandite. The starting material for SYNROC D (high Fe, high Al and composite compositions) is simulated sludge obtained in 55 gallon quantities from Southwestern Chemical Corporation. Hot pressing temperatures for SYNROC D are 1000-1150°C. Hot pressing tempertatures for hollandite are 1200-1400°C.

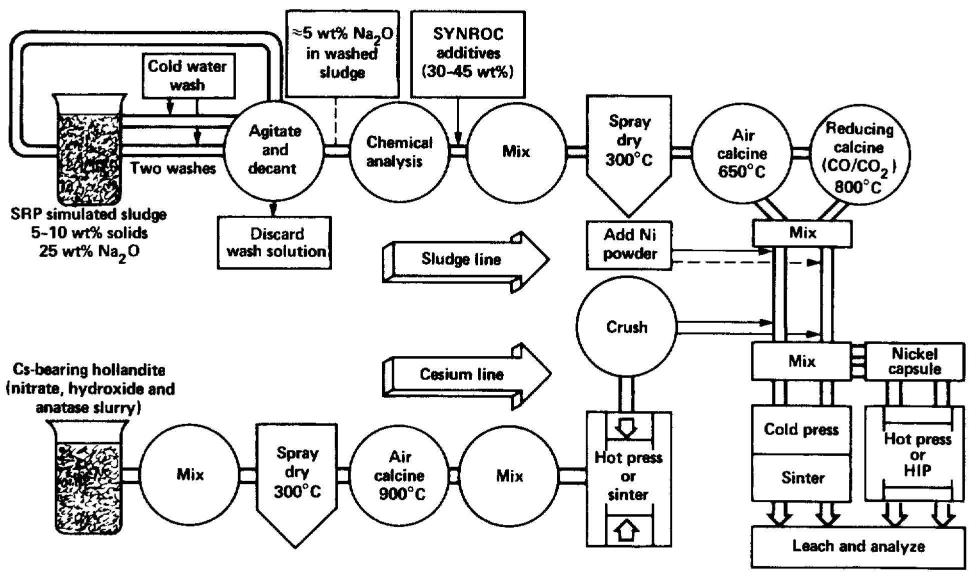

Fig. 4. Flow Diagram for Laboratory Scale Production of SYNROC D

REFERENCES

1. A. E. Ringwood, Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy, Australian National University Press, 64 p., (1978).

2. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization, Geochem. Journ., 13, 141-165, (1979).

3. A. E. Ringwood, S. E. Kesson, and N. G. Ware, Immobilizaton of U.S. Defense Nuclear Waste Using the SYNROC Process, in: Scientific Basis for Nuclear Waste Management, 2, C. Northrup, ed (1980).

4. J. A. Stone, S. T. Goforth, Jr., and P. K. Smith, Preliminary Evaluation of Alternative Forms for Immobilization of Savannah River Plant High-Level Waste, DP-1545, DuPont Savannah River Laboratory, 98p., (1979).

5. J. A. Stone, J. A. Kelley, and T. S. McMillan, Sampling and Analysis of SRP High-Level Waste Sludges, DP-1399, DuPont Savannah River Laboratory, 50p., (1976).

6. A. E. Ringwood, Personal Communication (1980).

7. P. Angelini, D. P. Stinton, R. W. Carpenter, J. S. Vavruska and W. J. Lackey, Phase Identification and Partitioning of Elements in Sol-Gel-Derived SYNROC, Amer. Cer. Soc. Bull., 59, 394, (1980).

8. D. G. Coles and F. Bazan, Continuous-Flow Leaching Studies of Crushed and Cored SYNROC, UCRL-84679, University of California, Lawrence Livermore National Laboratory, 29p., (1980).

9. C. Hoenig, R. Otto, F. Bazan, R. Rozsa, J. Grens, R. Lim, and G. Smith, Preparation History and Analytical Results for SYNROC C Powders. UCID publication, University of California, Lawrence Livermore National Laboratory, (in press)